

Optical recording medium

Publication number: CN1340811

Publication date: 2002-03-20

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Classification:

- international: G11B7/0045; G11B7/005; G11B7/013; G11B7/24;
G11B7/247; G11B7/248; G11B7/125; G11B7/00;
G11B7/013; G11B7/24; G11B7/125; (IPC1-7);
G11B7/0045; G11B7/00; G11B7/24

- european: G11B7/0045R; G11B7/005R; G11B7/013D; G11B7/24;
G11B7/247; G11B7/248

Application number: CN20011025457 20010704

Priority number(s): JP20000202149 20000704; JP20000202150 20000704

Also published as:

-  EP1170741 (A2)
-  US6808778 (B2)
-  US2002034604 (A)

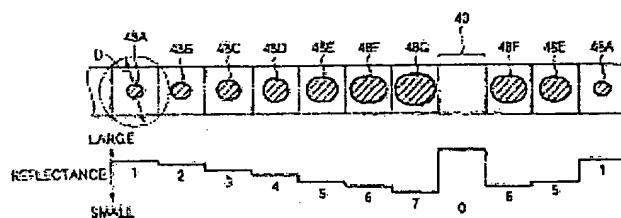
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Abstract not available for CN1340811

Abstract of corresponding document: EP1170741

An optical recording medium is provided with a recording layer and a reflecting film on an optically transparent substrate. The principal component of the recording layer is a dye. Virtual recording cells are assumed within grooves on the recording layer and recording marks with five different levels or more of increasing size (48A-G) are formed on each of the virtual recording cells by modulating the irradiation time of the laser beam in five levels or more in correspondence to the information to be recorded. The reflectance of the virtual recording cells modulates in many levels and the reflection level of the reading laser beam during regeneration is changed in five levels or more. The optically transparent substrate is made of a plastic with a glass transition point (Tg) of 160 DEG C or less. The reflecting film is a metal with a coefficient of thermal conductivity of 300k/W. m<-1> . K<-1> or more and a film thickness of 50nm or more.

FIG.3



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Optical recording medium

Description of corresponding document: EP1170741

[0001] The present invention relates to an optical recording medium that switches either the irradiation time or the irradiation power of a laser beam in many levels in correspondence to data used in the recording, irradiates the recording layer with the laser beam and then records the data in multiple levels.

[0002] A great deal of research has been carried out related to methods to record multiple pieces of data in signals with identical length by switching the depth of a regeneration signal (modulation factor of reflection signal) in many levels in contrast to methods to record data by changing the length of a regeneration signal (length of the modulated part of the reflection signal) in many levels with conventional optical recording mediums such as CD-R or DVD-R which are provided with recording layers and reflecting films, in this order, on an optically transparent substrate.

[0003] According to this optical recording method, because it is possible to record multiple pieces of data in the direction of depth compared to when binary data is recorded depending on the presence or absence of only a pit, the amount of signals assigned to fixed lengths can be increased. Consequently, optical recording methods which use holographs or optical recording mediums with multiple recording layers have been proposed in order to improve the linear recording density.

[0004] Hereupon, a case wherein data is recorded in many levels using a depth variation of the reflectance is called multilevel recording.

[0005] In this type of multilevel recording the recording marks must be shortened in order to improve the recording density.

[0006] Multilevel recording is, however, difficult when attempting to reduce the recording marks smaller than the beam diameter of a converged laser used for recording and reading.

[0007] For example, Japanese Patent Laid-Open Publication No. Hei. 10-134353 describes a method in which the quantity of laser light is adjusted in order to record multiple levels. In this method a regeneration signal is formed by differences in the reflection of the recording part and the non-recording part when the recording medium is a dye film or a phase-changing film. Consequently, in the method in Japanese Patent Laid-Open Publication No. Hei. 10-134353, the non-recording level and the recording level depend on a relationship of whether or not a recording exists and are not suitable for recording in many levels. Stated more clearly, nothing exists in the intermediate state between recording and non-recording for a phase-changing film or a dye film.

[0008] Up to the present the reason why multilevel recording in many levels was possible by means of modulating the quantity of laser light using a dye film or a phase-changing film as the recording medium was mainly due to the fact that the widths of the recording marks were changed by changing the power of the laser.

[0009] A converging beam normally forms a Gaussian distribution although when the recording film is a dye film or a phase-changing film, the recording is performed on the portion that exceeds a certain threshold value. Changing the power of the laser changed the spot size of the converging beam that can record which in turn changed the width of the recording marks.

[0010] If, however, the length of the recording marks are shortened to increase the recording density, it becomes difficult to perform multilevel recording in many levels, in particular in five levels or more, using a method that modulates the power of the laser to change the recording mark width. In other words, changing the recording power makes it difficult to change the reflection level during a regeneration in five levels or more.

[0011] Normally, the diameter of the converging beam is expressed by $K \lambda / NA$ (K : constant, λ : laser wavelength, NA : numerical aperture). Normal values for a pickup used in a CD are $\lambda = 780$ nm, $NA = 0.45$ with a diameter of approximately $1.6 \mu m$. For this case, if the recording mark length was $1.6 \mu m$ or less, it is difficult to perform multilevel recording in five levels or more using a conventional method that changes the laser power.

[0012] Further, there is an example of an optical recording medium as disclosed in Japanese Patent Laid-Open Publication No. Hei. 1-182846 wherein the absorbance of the reactive material in the recording layer

changes as a digital value when a quantity of incident light is supplied as a digital value.

[0013] The absolute value of the absorbance change is presumed to be very small for this optical recording medium however and has not yet attained practical use.

[0014] Furthermore, an optical recording method is disclosed in Japanese Patent Laid-open Publication No. Sho. 61-211835 in which the intensity or irradiation frequency of the irradiation light irradiating a photochromic material is changed in order to record at different arbitrary coloring density states.

[0015] In this optical recording method there is a problem in which the coloring density state cannot be read in five levels of more when irradiating and scanning laser light.

[0016] The rapid occurrence of thermal decomposition of dyes in optical recording mediums used as a recording materials which use dye as the principal material was considered to be favorable in conventional recording methods. This is because the signal quality is better due to the clear boundary between the recording part and the non-recording part.

[0017] If, however, there is rapid decomposition of the dye material during multilevel recording, decomposition of the dye will suddenly begin when a specified laser irradiation time or irradiation power is exceeded making it difficult to control the recording in many levels required for multilevel recording.

[0018] The inventor has discovered that it is possible to perform multilevel recording in five levels or more by means of changing the irradiation time or the irradiation power of the laser when the recording mark length is shorter than the diameter of the converging beam. The inventor has also discovered that a dye material that changes gradually is more suitable as a material for a recording film than a phase-changing material that changes quickly from non-recording to recording following temperature increases in the laser irradiation.

[0019] Furthermore, the inventor has found out it is possible to favorably perform multilevel recording by stipulating the thermal decomposition characteristics of the dye material.

[0020] At this point the thermal energy absorbed by the recording film will grow larger in line with lengthening of the laser irradiation time and/or increases in the laser irradiation power. If the thermal energy exceeds a certain threshold value, the dye will decompose and deteriorate and recording will be performed on the recording film. Excessive thermal energy that exceeds the threshold value passes through the reflecting film and diffuses around the edge. For example, if the diffusion of the thermal energy is insufficient for an optical recording medium such as a CD-R, unfavorable effects will occur such as deformation of the substrate or the guide tracks cut into the substrate.

[0021] Taking the above-mentioned issues into consideration, an object of the present invention is to provide an optical recording medium that utilizes a widely used optical recording medium, such as CD-R, to perform multilevel recording in many levels and can obtain favorable signal quality. In particular, to provide an optical recording medium that prevents deformation of the optically transparent substrate or the channels cut into the substrate used to guide the laser as well as prevent degradations in the recording signals due to deformation of the protective film on the reflecting film by making the diffusion of the thermal energy by the laser irradiation sufficient and/or by controlling the thermal decomposition characteristics of the dye material. In addition, an object of the present invention is to provide an optical recording medium that can favorably perform multi-level recording control.

[0022] The inventor has diligently conducted research on an optical recording medium and discovered a recording method that performs multilevel recording on this optical recording medium, and also verified that this recording method can perform high-density multilevel recording in five levels or more on this optical recording medium. Furthermore, the inventor has performed various types of experiments and found that stipulating the material properties of the optically transparent substrate and the coefficient of thermal conductivity and film thickness of the reflecting film was important for thermal diffusion. In addition, the inventor has found that if a dye whose thermal decomposition exceeds a range extending over 100 DEG C or more is used, favorable recording becomes possible extending over the time when the laser irradiation time goes from short to long and/or extending over the time when the laser irradiation power goes from low to high. Even further, the inventor has found that if a dye whose thermal decomposition starts at 300 DEG C or less is used, high sensitive recording becomes possible through which the inventor has completed the present invention.

[0023] In other words, the above-mentioned objectives are achievable by means of the present invention as follows.

[0024] (1) An optical recording medium, having a recording layer, whose principal component is a dye, provided on an optically transparent substrate, and a reflecting film formed on the recording layer, the medium being able to record information by irradiating a laser beam to form recording marks on said recording layer and read the recorded information by irradiating a reading laser beam onto the recording mark; wherein said recording layer has a virtual recording cell specified in an arbitrary unit length in a direction of relative movement between the laser beam and the recording layer and in a unit width in a direction that intersects said direction of movement at a right angle and continuously set in said direction of movement; said recording layer at said virtual recording cell can form recording marks with different sizes in correspondence to either a modulation of an irradiation time of the laser beam or an irradiation power in five levels or more; this allows multilevel recording of five levels or more of information by means of modulating the reflectance based on the area ratio of said recording marks to said virtual recording cells and transmittance, at least the area ratio; said optically transparent substrate is made of a thermoplastic resin with a glass transition point (Tg) of between 80 DEG C and 160 DEG C; said reflecting film is a metal with a coefficient of thermal conductivity of 300k/W . m<-1> . K<-1> or more and a film thickness at the recording mark of 50 nm or more.

[0025] (2) The optical recording medium according to (1), wherein said reflecting film material is characterized by the product of the coefficient of thermal conductivity and the film thickness being $2 \times 10^{-5} \text{ k/W} \cdot \text{K}$ or more.

[0026] (3) An optical recording medium, having a recording layer, whose principal component is a dye, provided on an optically transparent substrate, the medium being able to record information by irradiating a laser beam to form recording marks on said recording layer and read the recorded information by irradiating a reading laser beam onto the recording mark; wherein said recording layer has a virtual recording cell specified in an arbitrary unit length in a direction of relative movement between the laser beam and the recording layer and in a unit width in a direction that intersects said direction of movement at a right angle and continuously set in said direction of movement; said recording layer at said virtual recording cell can form recording marks with different sizes in correspondence to either a modulation of an irradiation time of the laser beam or an irradiation power in five levels or more; this allows multilevel recording of five levels or more of information by means of modulating the reflectance based on the area ratio of said recording marks to said virtual recording cells and transmittance, at least the area ratio; the dye used in said recording layer is made in such a manner that differences in a weight reduction start temperature due to thermal decomposition (TG) and a temperature when a weight thereof becomes 20% of an original weight thereof extends over a range of 100 DEG C or more.

[0027] Using a material with a coefficient of thermal conductivity of 300k/W . m<-1> . K<-1> as the reflecting film material in the present invention or setting the thickness of the reflecting film to 50 nm or less results in excessive heat causing deformation of the substrate or the channels cut into the substrate used to guide the laser as well as deformation of the protective film on the reflecting film leading to degradations in the recording signals.

[0028] This effect is dependent on the glass transition temperature of the substrate material on which laser guide grooves are provided. When a material with a high glass transition temperature, such as glass, is used as the material, deformation due to heat is not apparent. If a material with a glass transition temperature between 80 DEG C and 160 DEG C is used, this effect was found to be quite evident.

[0029] This thermal diffusion effect was also verified to be especially large during multilevel recording with adjacent recording marks in the recording direction.

[0030] These effects were present due to heat that occurred while recording in optical recording mediums used up to the present. However, it is assumed that even greater effects would more easily occur due to recording marks being placed adjacent in a linear direction in order to improve the recording density in the multilevel recording method.

[0031] Further, the size of the recording marks stated here refers to the size of changes in the quantity when the material constituting the recording layer decomposes and deteriorates due to irradiation of the laser beam to change the refractive index thereof or when the transmittance is changed due to the size in the direction of thickness when the refractive index changes.

[0032] In the present invention the reflectance could be controlled in many levels by means of specifying a dye constituting the recording layer.

[0033] Further, the optical recording medium may be constructed as follows.

[0034] (4) The optical recording medium according to (3), wherein said dye is characterized by weight

reduction due to said thermal decomposition starting at 300 DEG C or less and continuing until 350 DEG C or more.

[0035] (5) The optical recording medium according to (3), wherein a reflecting film is provided on said recording layer on a side opposite to a side on which the laser beam is incident, said optically transparent substrate is made of a thermoplastic resin with a glass transition point (Tg) of between 80 DEG C and 160 DEG C, and said reflecting film is a metal with a coefficient of thermal conductivity of 300k/W . m<-1> . K<-1> or more and a film thickness on a recording mark of 50 nm or more.

[0036] (6) The optical recording medium according to (5), wherein said reflecting film material is characterized by the product of the coefficient of thermal conductivity and the film thickness being $2 \times 10^{-5} \text{ k/W . K}^{-1}$ or more.

[0037] (7) The optical recording medium according to (4), wherein a reflecting film is provided on said recording layer on a side opposite to a side on which the laser beam is incident, said optically transparent substrate is made of a thermoplastic resin with a glass transition point (Tg) of between 80 DEG C and 160 DEG C, and said reflecting film is a metal with a coefficient of thermal conductivity of 300k/W . m<-1> . K<-1> or more and a film thickness on a recording mark of 50 nm or more.

[0038] (8) The optical recording medium according to (7), wherein said reflecting film material is characterized by the product of the coefficient of thermal conductivity and the film thickness being $2 \times 10^{-5} \text{ k/W . K}^{-1}$ or more.

[0039] (9) The optical recording medium according to any one of (1)-(8), wherein the unit length of said virtual recording cell is set almost equal to the length of the recording mark formed by laser beam irradiation for the maximum amount of time.

[0040] (10) The optical recording medium according to any one of (1)-(9), wherein: grooves for guising laser beam are provided along said recording layer, said virtual recording cells are set inside said grooves and said unit width matches a width of said groove.

[0041] (11) The optical recording medium according to any one of (1)-(10), wherein said unit length in said virtual recording cells are equal to or less than the diameter of beam waist of said reading laser beam.

[0042] (12) The optical recording medium according to any one of (1)-(11), wherein information is recorded in multiple levels in advance on one part of said recording layer.

[0043] (13) The optical recording medium according to any one of (1)-(12), wherein specific information which represents a multilevel recording medium is recorded on at least one of said virtual recording cells and a multilevel recorded part.

[0044] (14) The optical recording medium according to any one of (1)-(13), wherein grooves for guiding laser beam are provided along said recording layer and are cut in the middle.

[0045] Fig. 1 is a partial cross-sectional perspective view showing principle parts of an optical recording medium according to an embodiment of the present invention.

[0046] Fig. 2 is a block diagram showing an optical recording device that uses a laser beam to record information on the optical recording medium.

[0047] Fig. 3 is a model view showing the relationship between a recording mark, a virtual recording cell and the optical reflectance thereof when forming the recording mark on a recording layer by means of the optical recording device.

[0048] Fig. 4 is a partial perspective view showing a case when a laser beam that irradiates a virtual recording cell forms another shape.

[0049] Embodiments of the present invention will be now described in detail with reference to the drawings.

[0050] An optical recording medium 10 according to the embodiment of the present invention is a CD-R that uses a dye on a recording layer 12 and is composed of an optically transparent substrate 14 including a transparent substrate material, the recording layer 12 composed of a dye coated on and covering the grooves 16 used to guide the laser beam formed on one surface of the optically transparent substrate 14 (upper surface in Fig. 1), a reflecting film 18 whose principal component is gold or silver or an alloy

comprising these formed by sputtering or vacuum deposition on the upper side of the recording layer 12, and a protective layer 20 that covers the outside of the reflecting film 18. Irregularities (pre-grooves or pits) which represent information such as the grooves 16 or address signals are formed on the optically transparent substrate 14.

[0051] The optically transparent substrate 14 is a thermoplastic resin with a glass transition point (Tg) of between 80 DEG C and 160 DEG C and can be freely selected from among various types of materials being used in conventional optical recording mediums. For example, resins which can be used include a polycarbonate resin, polymethylmethacrylate resin, epoxy resin, polyolefin resin, and polyester resin. Further, the glass transition point is regulated by, for example, differential thermal analysis set forth in JIS K7121.

[0052] The principal component of the recording layer 12 on the optically transparent substrate 14 is an organic dye. The dyes which can be used for this organic dye include cyanine dye, squarylium dye, croconium dye, anthraquinone dye, metal containing azo dye, phthalocyanine dye and naphthoquinone dye. From among these various dyes a dye having a difference between the weight reduction start temperature due to thermal decomposition (TG) in an inert gas atmosphere and the temperature when the weight becomes 20% of the original weight extending over a range of 100 DEG C or more can be used. In addition, weight reduction due to thermal decomposition of the dye starts at 300 DEG C or less and continues until 350 DEG C or more.

[0053] The decomposition temperature of the dye can be controlled by introducing various types of polar groups including alkyl group, alkoxide group, allyl group, halogen atoms, alkylcarbonyl group, alkyl sulfonyl group, alkyl sulfonamide group, cyano group and nitro group or by changing the counter-ion composition in the ionic dyes.

[0054] The following materials can be used as a solvent for the organic dye coating solution: esters such as butyl acetate and cellosolve acetate; ketones such as methyl ethyl ketone, cyclohexanone and methyl isobutyl ketone; chlorinated hydrocarbons such as dichloromethane, 1,2-dichloro ethane and chloroform; amides such as dimethylform amide; hydrocarbons such as cyclohexane; ethers such as tetrahydofuran, ethyl ether and dioxane; alcohols such as ethanol, n-propanol, isopropanol, n-butanol and diacetone alcohol; fluorine solvents such as 2,2,3,4-tetrafluoro propanol; and glycol ethers such as ethyleneglycol monomethyl ether, ethyleneglycol monoethyl ether and propyleneglycol monomethyl ether. These solvents can be used independently or in combination taking into consideration solubility of the organic dyes being used. Various types of additives such as singlet oxygen quenchers, antioxidants, UV absorbents, plasticizers or lubricants may be further added to the coating solution depending on the purpose.

[0055] The reflecting film 18 on the recording layer 12 is a metal with a coefficient of thermal conductivity of $300\text{ k/W} \cdot \text{m}^{-1}$ or more at a normal temperature (approximately 20 DEG C). This metal is gold, silver or copper, or an alloy thereof. The reflecting film 18 is formed by a sputtering method or a vacuum deposition method. The thickness of the reflecting film 18 is 50 nm or more at the area where a recording mark (described later) is formed and is preferably 60 SIMILAR 300 nm thick. Further, the product of the coefficient of thermal conductivity and the film thickness of the material used for the reflecting film 18 is set to be $2 \times 10^{-5} \text{ k/W} \cdot \text{K}^{-1}$ or more.

[0056] The protective layer 20 is provided on the reflecting film 18 for the purpose of physically and chemically protecting the organic dye recording layer 12 and the reflecting film 18. The protective layer can also be provided to improve the anti-scratch properties and excess moisture tolerance on the side of the optically transparent substrate 14 where the organic dye recording layer 12 is not provided.

[0057] Generally, UV curable resins are widely used for the protective layer 20 material. After preparing a coating solution of this UV curable resin as is or by dissolving in a suitable solvent, the protective layer 20 is formed by coating the coating solution onto the optically transparent substrate 14 and then irradiating ultraviolet light to harden the solution. Depending on the objective, various different additives such as an antistatic additive, an antioxidant and an ultraviolet absorbent can be added to this coating solution. The layer thickness of the protective layer 20 is approximately 0.1 SIMILAR 100 μm .

[0058] Multilevel recording onto the optical recording medium 10 obtained in this manner is performed by means of the optical recording apparatus 30 shown in Fig. 2.

[0059] The recording onto the optical recording medium 10 is performed using, for example, a semiconductor laser beam as the recording light that has a wavelength in a range of 770 SIMILAR 790 nm or a wavelength in a range of 630 SIMILAR 660 nm to deteriorate an organic dye by irradiating a suitable laser beam onto the organic dye recording layer 12 while rotating the optical recording medium 10 at a fixed linear velocity or at a fixed-angle velocity. Data regeneration is performed by reading differences in

the amount of reflected laser light at areas when the organic dye deteriorated and areas where it did not.

[0060] The optical recording apparatus 30 is a CD-R recorder. This recorder records information by means of a laser beam from a laser 36 while rotating the optical recording medium (disk) 10 by a spindle motor 32 at a fixed linear velocity or at a fixed-angle velocity via a spindle servo 31 onto the recording layer 12 formed as described above on the optical recording medium (disk) 10.

[0061] The laser 36 is designed to use the laser driver 38 to control the laser beam irradiation time, namely, the number of laser pulses, for each of the virtual recording cells 40 (described later) shown in Fig. 1 and Fig. 3 depending on the information to be recorded.

[0062] Reference numeral 42 in Fig. 2 designates a recording optical system that includes an objective lens 42A and a half mirror 42B. Focus tracking control is performed by a focus tracking servo 44 in order that the objective lens 42A converges the laser beam on the recording layer 12. Further, The objective lens 42A and the half mirror 42B are controlled and moved by a feed servo 46 at a fixed speed from the outer periphery to the inner periphery in phase with the rotation of the disk 10.

[0063] The spindle servo 31, laser driver 38, focus tracking servo 44 and feed servo 46 are controlled by a control apparatus 50. Data (information) to be recorded onto the recording layer 12 is entered into the control apparatus 50.

[0064] Next, the virtual recording cell 40 and the recording marks recorded on the virtual recording cell 40 will be described.

[0065] These virtual recording cells are specified in unit widths in the radial direction and unit lengths in the rotational direction of a recording medium. A unit width is a width equal to or less than the diameter of the beam waist of the laser beam and can be freely selected from among the track pitch or groove width of the disk 10.

[0066] As shown in Fig. 1, the virtual recording cells 40 of this embodiment are assumed to be continuous circumferentially inside the groove 16 and have a length (circumferential length) shorter than the beam diameter D (diameter of beam waist) in the rotational direction, circumferentially, of the disk 10. In addition, the width is set equal to the groove 16. The laser beam is irradiated onto each virtual recording cell 40 forming the recording marks 48A SIMILAR 48G in response to the information to be recorded as shown in typical fashion in Fig. 3.

[0067] Here, the beam diameter D of the laser beam emitted from the laser 36 at the position of the recording layer 12 grows larger than the virtual recording cell 40. Depending on the material selected for the recording layer 12, however, the recording marks 48A SIMILAR 48G can be formed with different diameters at the center of the laser beam in response to the laser irradiation time (The laser beam is circular although, since the beam irradiates while the optical recording medium is rotating, the recording marks form long circular shapes in response to the irradiation time.).

[0068] Because the focused laser beam normally forms a Gaussian distribution, recording is only performed at the portion where the threshold value of the irradiation energy of the laser beam is exceeded on the recording layer 12. Because of this, the spot size of the laser beam that can record on the recording medium changes due to changes in the irradiation time of the laser beam. This, for example, can form seven levels of recording marks 48A SIMILAR 48G as shown in Fig. 3.

[0069] Here, the dye constituting the recording layer 12 is specified as described above. Since decomposition and deterioration do not rapidly occur relative to the irradiation time of the laser beam, favorable multilevel recording is possible.

[0070] The size of each of the recording marks 48A SIMILAR 48G is set such that the reflectance of the reflecting light when the reading laser beam irradiates the virtual recording cells 40 becomes seven levels. The reflectance grows larger as the recording marks grow smaller. The maximum reflectance is present at virtual recording cells where recording marks are not formed and the minimum reflectance is present at virtual recording cells where the largest recording mark 48G is formed.

[0071] In more detail, the reflectance is set taking into consideration the area ratio for each of the recording marks 48A SIMILAR 48G relative to the virtual recording cells 40 and the transmittance of the recording marks themselves.

[0072] The transmittance of the recording marks 48A SIMILAR 48G themselves differs because the material constituting the recording layer 12 decomposes and deteriorates due to irradiation of the laser

beam to change the refractive index or because the quantity of the recording layer 12 in the thickness direction changes. If the transmittance of the recording mark portion that was formed is zero, there is no need for this consideration.

[0073] At this time, a material with a coefficient of thermal conductivity of 300W/mK or more is used as the material for the reflecting film 18. The thickness of the reflecting film 18 is 50 nm or more. Further, a material with a glass transition point (T_g) of between 80 DEG C and 160 DEG C is used for the optically transparent substrate 14. Consequently, there is no excessive heat due to the laser beam irradiation causing deformation of the optically transparent substrate 14, the grooves 16 used to guide the laser cut into the optically transparent substrate 14 or the protective layer 20 on the reflecting film 18. Thus, there is no degradation in the recording signals.

[0074] In the embodiment described above, although the irradiation time of the laser beam is changed in five levels or more to perform multilevel recording on the recording layer 12, the present invention is not limited to this. The irradiation power of the laser beam or the irradiation time and irradiation power can be changed.

[0075] Although in this embodiment the optical recording medium 10 is a CD-R disk as described above, the present invention is not limited to this and normally can be applied to another optical recording medium.

[0076] The example in the embodiment described above is an example of the optical recording medium 10 whereon information such as data is not recorded although the present invention is not limited to this. The present invention can also be applied to an optical recording medium onto which multilevels of information has been recorded in five levels or more.

[0077] Even further, the size of the virtual recording cells 40 set in the recording layer 12 when forming recording marks by means of the optical recording apparatus 30 is not limited to the example in this embodiment but can be any length equal to or less than the diameter of the beam waist of the laser beam. In addition, although the size of the virtual recording cells 40 can be freely set for an optical recording medium not provided with the grooves 16, it is preferable to set the virtual recording cells 40 to a length almost equal to the recording marks formed when the irradiation energy at the point where laser beam is at its longest irradiation time exceeds the threshold value that provides changes to the recording layer 12.

[0078] The laser beam mentioned above forms a circular shape at the position of the recording layer 12. As shown in Fig. 4 however, this can utilize, for example, a beam shaping prism 42C in addition to the objective lens 42A and the beam shape can be short in the feed direction of the recording medium 10 and a long ellipse or a linear shape at a right angle to this. For this case, because the recording marks 49 become shorter, the virtual recording cells can also be made shorter. In other words, the recording density can be improved.

[0079] As designated by reference numeral 52 in Fig. 1, by means of either having in advance a plurality of pits with a number of different reflectances matching the number of levels of the signal modulation or by performing multilevel recording as described above in advance on a portion of the optical recording medium, the recording medium 10 has information that separately identifies the recording medium at the recording marks 54 of these plurality of pits 52 and/or the portions where multilevel recording is complete, information that identifies an optical recording medium for use with multilevel recording, and specific information such as information that determines the laser beam power needed to record/regenerate the recording medium. This specific information can reliably identify an optical recording medium for use with multilevel recording by means of regeneration of the optical recording medium and/or reading data for recording as well as separately identify these and determine the number of levels of the laser beam power in response to the number of pits already recorded. Because of this, even more reliable multilevel recording and regeneration is possible. In addition to this, as designated by reference numeral 56 in Fig. 1, the same effect can be achieved by means of providing a groove interruption part that cuts the groove of laser beam guides in the middle. These methods can be used independently or combined.

[Example]

[0080] In the following examples 1 SIMILAR 9 of the present invention will be described in comparison to comparative examples 1 SIMILAR 6. Here a CD-R that used a dye on the recording layer 12 was utilized as the optical recording medium 10 to carry out experiments on multilevel recording.

[Example 1]

[0081] Cyanine dye was dissolved into a fluoridated alcohol to prepare a 2% coating solution used to form a recording layer. A spin coat method in which the rpm was varied from 200 rpm up to 5000 rpm was used to coat this coating solution onto the surface of a pre-groove side of an optically transparent substrate with a diameter of 120 mm and a thickness of 1.2 mm that was composed of a polycarbonate resin (Teijin Kasei Inc.: Panlight AD5503) whereon a spiral-shaped pre-groove (track pitch: 1.6 μ m, pre-groove width 0.35 μ m, pre-groove depth 0.18 μ m) was formed by means of injection molding. This process formed an organic dye recording layer approximately 200 nm thick from the bottom of the inside of the pre-groove. The glass transition temperature of the polycarbonate was 140 DEG C.

[0082] Next, a sputtering method was utilized to form an Ag (coefficient of thermal conductivity of silver is 427k/W . m<-1> . K<-1>; chronological table of science) reflecting film approximately 50 nm thick on the organic dye recording layer. In addition, a spin coat method in which the rpm was varied from 300 rpm up to 4000 rpm was used to coat a UV curable resin (Dainippon Ink Kagaku Kogyo Inc.: SD318) onto this reflecting film. After the coating was completed, ultraviolet rays were irradiated by a mercury vapor lamp from above the coating film to form a 10 μ m thick protective layer.

[0083] Multilevel recording was then attempted using the optical recording medium obtained in this manner. Multilevel recording was performed by means of changing the time the laser beam irradiates the optical recording medium in six levels while rotating the optical recording medium at a fixed linear velocity. Regeneration was performed by means of irradiating a 1 mW laser beam while rotating the optical recording medium at the same fixed linear velocity and then detecting differences in the reflected amount of light. The device used to evaluate the recording was a DDU (laser wavelength = 784 nm) manufactured by Pulstec Industrial Co., Ltd. and the laser beam power while recording was 14 mW. The recording linear velocity was 4.8 m/sec and the clock frequency of the recording was 4 MHz (250 nsec).

[0084] The laser irradiation times while recording onto the optical recording medium were (1) 50 nsec, (2) 80 nsec, (3) 110 nsec, (4) 140 nsec, (5) 170 nsec, and (6) 200 nsec to perform multilevels recording. Each signal was recorded over a period of one revolution of the disk.

[0085] When recording was performed in this manner and the jitter values of the recorded signals were read in and measured using a digital oscilloscope LC-534EL manufactured by Le Croy Corp., fluctuations due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0086] Taking into consideration a case in which the recording is performed using a conventional binary recording and regeneration method in the measurement apparatus for jitter values being used here, it is possible to judge whether favorable recording is performed if the jitter value is 10% or less.

[Example 2]

[0087] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the film thickness of the Ag reflecting film was changed to 100 nm. The recording conditions were identical to example 1. Jitter values of the recorded signals were measured in the same manner.

[Example 3]

[0088] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the reflecting film material was changed to Au (coefficient of thermal conductivity of gold is 318k/W . m<-1> . K<-1>; chronological table of science). The recording conditions were identical to example 1. Jitter values of the recorded signals were measured in the same manner.

[Example 4]

[0089] An optical recording medium was produced in the same manner as example 3 and multilevel recording performed although the film thickness of the reflecting film was changed to 100 nm. The

recording conditions were identical to example 1. Jitter values of the recorded signals were measured in the same manner.

[Example 5]

[0090] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the reflecting film material was changed to Cu (coefficient of thermal conductivity of copper is $401\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$; chronological table of science). The recording conditions were identical to example 1. Jitter values of the recorded signals were measured in the same manner.

[Example 6]

[0091] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the optically transparent substrate material was changed to polyolefin (Zeon Corp.: ZEONEX280).

[0092] The glass transition temperature of the polyolefin was 123 DEG C.

[0093] The recording conditions were identical to example 1.

[0094] Jitter values of the recorded signals were measured in the same manner.

[Comparative example 1]

[0095] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the film thickness of the Ag film was changed to 40 nm.

[0096] Problems with the signal quality were found especially if the laser irradiation time was long when measuring the jitter value of the recorded signals in the same manner.

[Comparative example 2]

[0097] An optical recording medium was produced in the same manner as example 5 and multilevel recording performed although the film thickness of the Cu film was changed to 40 nm. The jitter value of the recorded signals was measured in the same manner.

[Comparative example 3]

[0098] An optical recording medium was produced in the same manner as example 2 and multilevel recording performed although the reflecting film was changed to Al (coefficient of thermal conductivity of aluminum is $237\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$; chronological table of science).

[0099] Jitter values of the recorded signals were measured in the same manner.

[Comparative example 4]

[0100] An optical recording medium was produced and multilevel recording performed in the same manner although the substrate material was changed to glass. The pre-groove configuration on the glass was the same as example 1 and a plasma etching method was used as the method to form the grooves. The recording conditions were identical to example 1. Jitter values of the recorded signals were measured in the same manner.

[0101] The relationship between the jitter values, reflecting film characteristics and laser irradiation time in

the above results are shown in Table 1.

EMI33.1

[Example 7]

[0102] An organic dye recording layer approximately 200 nm thick was formed under conditions identical to example 1 in which cyanine dye A used is as shown in the chemical formula below. A substrate on which a discrimination signal to indicate that the optical recording medium is being used for multilevel recording and information signals related to the laser beam irradiation time were recorded in advance was used for the optically transparent substrate used here.

EMI34.1

[0103] Next, a sputtering method was utilized to form an Ag reflecting layer approximately 100 nm thick on the organic dye recording layer. A spin coat method in which the rpm was varied from 300 rpm up to 4000 rpm was used to coat a UV curable resin (Dainippon Ink Kagaku Kogyo Inc.: SD318) onto this reflecting layer. After the coating was completed, ultraviolet rays were irradiated by a mercury vapor lamp from above the coating film to form a 10 mu m thick protective layer.

[0104] When multilevel recording was performed under conditions identical to example 1 using the optical recording medium obtained in this manner and the jitter values was measured, fluctuations due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0105] When thermal decomposition temperature measurements of this cyanine dye A were performed using a 2050 measurement device manufactured by TA Instrument Corp. at a temperature increase state of 10 DEG C / minute within a nitrogen atmosphere, the decomposition start temperature was 230 DEG C and the temperature when the weight became 20% of the original weight (decomposition end temperature) was 480 DEG C. Further, weight reductions in the cyanine dye due to thermal decomposition started at 300 DEG C or less and then continued until 350 DEG C or more.

[Example 8]

[0106] An optical recording medium was produced in the same manner as example 1 and multilevel recording performed although the dye in example 7 was changed to a 1:1 mixture (mol ratio) of cyanine A and phthalocyanine B dyes and the coating solvent was changed from fluoridated alcohol to ethyl cellosolve.

[0107] The laser beam power while recording was set to 13 mW. The linear recording velocity at this time was 4.8 m/s and the clock frequency for the recording was 4 MHz (250 nsec). The laser irradiation times while recording were (1) 50 nsec, (2) 70 nsec, (3) 90 nsec, (4) 110 nsec, (5) 130 nsec, and (6) 150 nsec.

[0108] Each signal was recorded over a period of one revolution of the disk. When the recording was performed in this manner and the jitter values of the recorded signals were read in and measured using a digital oscilloscope LC-534EL manufactured by Le Croy Corp., fluctuations due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0109] During thermal decomposition measurements of this dye mixture the decomposition start temperature was 230 DEG C and the decomposition end temperature was 480 DEG C. Further, weight reductions in the dye mixture due to thermal decomposition started at 300 DEG C or less and then continued until 350 DEG C or more.

[Example 9]

[0110] An optical recording medium was produced in like manner to example 8 and multilevel recording performed although the dye in example 8 was changed to a 1:1 mixture (mol ratio) of cyanine A and phthalocyanine C dyes.

[0111] The laser beam power while recording was set to 13 mW. The linear recording velocity at this time was 4.8 m/s and the clock frequency for the recording was 4 MHz (250 nsec). The laser irradiation times while recording were (1) 50 nsec, (2) 70 nsec, (3) 90 nsec, (4) 110 nsec, (5) 130 nsec, and (6) 150 nsec. Each signal was recorded over a period of one revolution of the disk.

[0112] When the recording was performed in this manner and the jitter values of the recorded signals were read in and measured using a digital oscilloscope LC-534EL manufactured by Le Croy Corp., fluctuations due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0113] During thermal decomposition measurements of this dye mixture the decomposition start temperature was 230 DEG C and the decomposition end temperature was 547 DEG C. Further, weight reductions in the dye mixture due to thermal decomposition started at 300 DEG C or less and then continued until 350 DEG C or more.

[Comparative example 5]

[0114] An optical recording medium was produced in the same manner as example 7 and multilevel recording performed although the dye in example 7 was changed to phthalocyanine B dye as shown in the chemical formula below and the coating solvent was changed to ethyl cellosolve.

[0115] The laser beam power while recording was set to 14 mW. The linear recording velocity at this time was 4.8 m/s and the clock frequency for the recording was 4 MHz (250 nsec). The laser irradiation times while recording were (1) 70 nsec, (2) 80 nsec, (3) 90 nsec, (4) 100 nsec, (5) 110 nsec, and (6) 120 nsec. Each signal was recorded over a period of one revolution of the disk.

EMI38.1

[0116] When the recording was performed in this manner and the jitter values of the recorded signals were read in and measured using a digital oscilloscope LC-534EL manufactured by Le Croy Corp., the jitter values were poor regardless of the differences in the laser beam irradiation time while recording.

[0117] During thermal decomposition measurements of this phthalocyanine B dye the decomposition start temperature was 319 DEG C and the decomposition end temperature was 414 DEG C.

[Comparative example 6]

[0118] An optical recording medium was produced in the same manner as example 7 and multilevel recording performed although the dye was changed to phthalocyanine C dye as shown in the chemical formula below and the coating solvent was changed to methyl cyclohexane.

EMI39.1

[0119] The laser beam power while recording was set to 14 mW. The linear recording velocity at this time was 4.8 m/s and the clock frequency for the recording was 4 MHz (250 nsec). The laser irradiation times while recording were (1) 70 nsec, (2) 80 nsec, (3) 90 nsec, (4) 100 nsec, (5) 110 nsec, and (6) 120 nsec. Each signal was recorded over a period of one revolution of the disk.

[0120] When the recording was performed in this manner and the jitter values of the recorded signals were read in and measured using a digital oscilloscope LC-534EL manufactured by Le Croy Corp., the jitter values were poor regardless of the differences in the laser beam irradiation time while recording.

[0121] During thermal decomposition measurements of this phthalocyanine C dye the decomposition start temperature was 510 DEG C and the decomposition end temperature was 546 DEG C.

[0122] Table 2 shows the results of the thermal decomposition characteristics of the dyes, laser irradiation times while recording and jitter values of recorded signals in examples 7-9, comparative examples 5 and 6, and examples 10 and 11 described later.

EMI40.1

[Example 10]

[0123] In contrast to the conditions in example 1, the dye was changed to phthalocyanine dye produced by Ciba [Super Green] and the coating solvent was changed to dimethyl cyclohexane to produce the optical recording medium by forming the organic dye recording layer, approximately 100 nm thick at the pre-groove location, on the optically transparent substrate having the pre-groove with a depth of approximately 100 nm and a width of approximately 600 nm.

[0124] As shown in Table 2, when multilevel recording was performed under conditions identical to example 1 using the optical recording medium obtained in this manner and the jitter values was measured, fluctuations in the jitter values due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0125] During thermal decomposition measurements of this dye the decomposition start temperature was approximately 263 DEG C and the decomposition end temperature was approximately 820 DEG C. In addition, weight reductions in the dye due to thermal decomposition started at 300 DEG C or less and then continued until 350 DEG C or more.

[Example 11]

[0126] In contrast to the conditions in example 1, the dye was changed to phthalocyanine dye produced by Yamada Chemicals [YDN-02] and the coating solvent was changed to a mixture of dimethyl cyclohexane, 2-methoxyethanol, methyl ethyl ketone and tetrahydorfuran and the concentration thereof was adjusted to 1.5 wt% to produce the optical recording medium by forming the organic dye recording layer, approximately 120 nm thick at the pre-groove location, on the optically transparent substrate having the pre-groove with a depth of approximately 160 nm and a width of approximately 650 nm.

[0127] As shown in Table 2, when multilevel recording was performed under conditions identical to example 1 using the optical recording medium obtained in this manner and the jitter values was measured, fluctuations in the jitter values due to differences in the laser beam irradiation time while recording were small and favorable results were obtained.

[0128] During thermal decomposition measurements of this dye the decomposition start temperature was approximately 242 DEG C and the decomposition end temperature was approximately 860 DEG C. In addition, weight reductions in the dye due to thermal decomposition started at 300 DEG C or less and then continued until 350 DEG C or more.

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[19] 中华人民共和国国家知识产权局

[51] Int. Cl⁷

D1

G11B 7/004

G11B 7/24 G11B 7/00

[12] 发明专利申请公开说明书

[21] 申请号 01125457.2

[43] 公开日 2002 年 3 月 20 日

[11] 公开号 CN 1340811A

[22] 申请日 2001.7.4 [21] 申请号 01125457.2

[30] 优先权

[32] 2000.7.4 [33] JP [31] 202149/2000

[32] 2000.7.4 [33] JP [31] 202150/2000

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权利要求书 2 页 说明书 19 页 附图页数 4 页

[54] 发明名称 光学记录介质

[57] 摘要

一种光学透光性基底上置有记录层和反射膜的光学记录介质。记录层 的最重要成分是染料。潜在记录单元被设定在记录层的槽内,根据待记录 信息以五级或更多级方式调节激光束照射时间,在每个潜在记录单元中形 成大小递增的五种不同级或更多级的记录标记。将潜在记录单元的反射比 以多级方式调节,而再生期间读取激光束的反射水平便按五级或更多级别 变化。光学透光性基底由 160℃ 或更低玻璃化转变点 (T_g) 塑料制成。反射膜 是导热系数 300k/W · m⁻¹ · K⁻¹ 或者更大的金属,薄膜厚度是 50nm 或更厚。

ISSN 1 0 0 8 - 4 2 7 4

权 利 要 求 书

1. 一种光学记录介质，具有记录层，其首要成分是染料，位于光学透光性基底上，并包括形成在记录层上的反射膜，这种介质通过照射激光束在所述的记录层上形成记录标记而记录信息，并通过照射读取激光束至记录标记上而读取记录信息；其中所述的记录层具有潜在记录单元，沿激光束和记录层之间相对移动方向确定该单元任意的单元长度，沿所述移动方向正交的方向确定该单元宽度，并且沿所述移动方向不断地安置；根据调整的激光束照射时间或者照射功率，以五级或更多级在所述记录层的所述潜在记录单元中可形成各种大小的记录标记；这允许多级记录五级或更多级的信息，通过调节以所述记录标记对所述潜在记录单元面积比为基础的反射比和透射比(至少是面积比)实现；所述光学透光性基底由玻璃化转变点(T_g)在 80°C 和 160°C 之间的热塑性树脂制成；所述的反射薄膜是金属的，系 $300\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大导热系数的金属，而记录标记的薄膜厚度为 50nm 或更厚。

2. 按照权利要求 1 的光学记录介质，其中所述反射膜材料特征在于导热系数和薄膜厚度的乘积是 $2 \times 10^{-5} \text{ k/W}\cdot\text{K}^{-1}$ 或者更大。

3. 一种光学记录介质，具有记录层，其首要成分是染料，位于光学透光性基底上，该介质可通过照射激光光束在所述的记录层上形成记录标记而记录信息，并通过在记录标记上照射读取激光束而读取记录的信息；其中所述的记录层具有潜在记录单元，沿激光束和记录层之间相对移动方向确定该单元任意单元长度，沿所述移动方向的正交方向确定该单元宽度，并且沿所述移动方向不断地安置；根据调整的激光束照射时间或者照射功率，以五级或更多级在所述记录层的所述潜在记录单元中可形成各种大小的记录标记；这允许多级记录五级或更多级的信息，通过调节以所述记录标记对所述潜在记录单元面积比为基础的反射比和透射比(至少是面积比)实现；所述记录层采用的染料以这样的方式制备出，即要使其由于热分解(TG)的重量减轻开始温度，与其重量变为开始重量的 20% 时温度之差延续 100℃ 范围或者更宽。

30 4. 按照权利要求 3 的光学记录介质, 其中所述染料特征在于因所

述热分解所致重量减少在 300°C 或稍低温度开始，并持续至 350°C 或更高。

5. 按照权利要求 3 的光学记录介质，其中反射膜设置于所述记录层上与激光入射侧相对的一侧，所述光学透光性基底是由玻璃化转变点
5 (Tg)在 80°C 和 160°C 之间的热塑性树脂制成；所述的反射薄膜是金属，其具有 $300\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大的导热系数，而记录标记上薄膜厚度为 50nm 或更厚。

6. 按照权利要求 5 的光学记录介质，其中所述反射膜材料特征在于导热系数和薄膜厚度的乘积是 $2 \times 10^{-5} \text{ k/W}\cdot\text{K}^{-1}$ 或者更大。

10 7. 按照权利要求 4 的光学记录介质，其中反射膜设置于所述记录层上与激光入射侧相对的一侧，所述的光学透光性基底是由玻璃化转变点(T_g)在 80°C 和 160°C 之间的热塑性树脂制成；所述的反射薄膜是金属，其具有 $300\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大的导热系数，而记录标记的薄膜厚度为 50nm 或更厚。

15 8. 按照权利要求 7 的光学记录介质, 其中所述反射膜材料特征在于导热系数和薄膜厚度的乘积是 $2 \times 10^{-5} \text{ k/W} \cdot \text{K}^{-1}$ 或者更大。

说 明 书

光学记录介质

5 发明背景

本发明涉及到一种光学记录介质，它根据记录中使用的数据，以多级方式转换激光束的照射时间或者照射功率，以激光束照射记录层，接着以多级方式记录数据。

有关通过多级转换再生信号的深度(反射信号的调制系数)，在具有相同长度的信号中记录多段数据的方法，人们已经开展了大量的研究，这与通过多级改变再生信号的长度(已调整部分的反射信号的长度)，以常规的光学记录介质例如 CD-R 或 DVD-R 记录数据的方法形成对照，该光学记录介质在光学透光性基底上依次具有记录层和反射膜。

按照这种光学记录方法，与仅仅依赖凹坑的存在与否记录二进制数据相比较，由于可以沿深度方向记录多段数据，由此可提高分配给固定长度的信号数量。结果，为了提高线性记录密度，人们已提出采用全息照相或者具有多层记录层的光学记录介质的光学记录方法。

于是，利用反射比的深度变化以多级方式记录数据的情况，称为多级记录。

20 此类型的多级记录中，必需缩短记录标记，以提高记录密度。

然而，当尝试缩小记录标记，使其小于用于记录和读取的聚焦激光的光束直径时，多级记录是困难的。

例如，日本专利公开 平 10-134353 描述了一种方法，其中调整激光的量以实现多级记录。在此方法中，当记录介质是染料薄膜或者相变薄膜时，记录部分和非记录部分的反射比的差异形成了再生信号。因此，在日本专利公开平 10-134353 的方法中，非记录级和记录级取决于有否记录存在，且不适于多级记录。更清楚地说来，对于相变薄膜或者染料薄膜，在记录和非记录之间没有中间状态存在。

30 直到现在，有许多级别的多级记录，通过采用染料薄膜或相变薄膜作为记录介质调整激光的参数可行的原因，主要归因于这样的事实，即

记录标记的宽度通过改变激光的功率而变化。

聚焦的光束通常形成高斯分布，尽管记录薄膜是染料薄膜或者相变薄膜，记录在超过某一阈值部分实施。改变功率的激光改变了聚焦光束的光点直径，它可记录依次改变的记录标记的宽度。

5 然而，采用调整激光功率的方法以改变记录标记的宽度时，如果使记录标记的长度缩短以提高记录密度，则以多级方式进行多级记录便变得困难，尤其是五级或者更多级。换言之，改变记录功率使得在五级或更多级的再生期间改变反射水平是困难的。

通常，聚焦的激光束的直径由 $K\lambda/NA$ 表示(K : 常数， λ : 激光波长，
10 NA : 数值孔径)。CD 中采用的拾音器(pickup)的正常值是 $\lambda=780\text{nm}$ ，
 $NA=0.45$ ，具有大约 $1.6\mu\text{m}$ 的直径。这种情况下，如果记录标记的长度是 $1.6\mu\text{m}$ 或者更短，采用常规的改变激光功率的方法以五级或更多级进行多级记录是困难的。

此外，日本专利公开平 1-182846 公开了光学记录介质的例子，其中
15 如果入射光量作为数值供给，则记录层活性物质的吸收率按数值变化。

然而由于认为这种光学记录介质吸收率的绝对值变化非常小，因而尚未获得实际使用。

此外，日本专利公开昭 61-211835 公开了一种光学记录方法，其中
20 改变照射光照射光致变色材料的强度或照射频率，以不同任意色密度状态进行记录。

在这种光学记录方法中，存在一个问题，即当照射和扫描激光时，以五级或更多级不可读取色密度状态。

光记录介质中用作记录材料的染料(采用染料作为首要的材料)的热分解迅速发生，在常规的记录方法中被认为是良好的。这是因为由于记录部分和非记录部分之间清楚的界限，使信号质量较好。
25

然而，如果在多级记录期间染料材料迅速分解，即当超过指定的激光照射时间或者照射功率时，染料的分解会突然开始，这使得多级记录需要的以多级方式控制记录更困难。

发明概述

30 本发明者已发现，当记录标记长度短于聚焦光束的直径时，通过改

变激光的照射时间或者照射功率以五级或更多级进行多级记录是可行的。本发明者也发现，与随着激光照射温度提高之后，从非记录至记录迅速变化的相变材料相比，逐渐改变的染料材料更适合作为记录薄膜材料。

5 此外，本发明者发现通过确定染料材料的热分解性质，良好地进行多级记录是可行的。

这里，经记录薄膜吸收的热能会较大增长，与延长激光照射时间或提高激光照射功率一致。如果热能超过一定的阈值，染料会分解和变质，在记录薄膜上会进行记录。过剩的超过阈值的热能经过反射薄膜并10 散射到边缘。例如，如果热能的散射对于光学记录介质例如 CD-R 是不充分的，有害的反应会发生，例如基底的变形或者导轨切入基底。

考虑到上述问题，本发明的一项目的是提供一种光学记录介质，它采用广泛使用的光学记录介质，例如 CD-R，以许多级别进行多级记录，并且可以获得良好的信号质量。尤其是，提供一种光学记录介质，它能15 防止光学透光性基底的变质或者避免使引导激光的槽切入基底，以及防止记录信号的降级，这种降级归因于激光充分照射的热能散射和/或染料材料的热分解性质的控制引起的反射薄膜上的保护膜变形。此外，本发明的一项目的是提供可良好进行多级记录控制的光学记录介质。

本发明者不懈地对光学记录介质进行过研究，并发明一种在此光学20 记录介质上进行多级记录的记录方法，并且亦证明这种记录方法可以以五级或者更多级在该光学记录介质上进行高密度多级记录。此外，本发明者已进行了各种类型的实验，并发现规定光学透光性基底的材料性质和反射膜的导热系数和薄膜厚度对于热扩散是重要的。此外，本发明者发现，如果采用热分解温度延续超过 100°C 或者更宽范围的染料，当激光25 照射时间从短至长变化时和/或当激光照射功率从低至高变化时，在此时间良好地记录可能延续。更进一步而言，本发明者发现如果采用的染料的热分解在 300°C 或者更低温度开始时，高灵敏记录是可能的，由此本发明者完成了本发明。

换言之，上述的目的通过如下的本发明方法可以达到。

30 (1) 一种光学记录介质，具有记录层，其首要成分是染料，位于光学

透光性基底上，并包括形成在记录层上的反射膜，这种介质通过照射激光束在所述的记录层上形成记录标记而记录信息，并通过照射读取激光束至记录标记上而读取记录信息；其中所述的记录层具有潜在记录单元，沿激光束和记录层之间相对移动方向确定该单元任意的单元长度，
 5 沿所述移动方向正交的方向确定该单元宽度，并且沿所述移动方向不断地安置；根据调整的激光束照射时间或者照射功率，以五级或更多级在所述记录层中的所述潜在记录单元中可形成各种大小的记录标记；这允许多级记录五级或更多级的信息，通过调节以所述记录标记对所述潜在记录单元面积比为基础的反射比和透射比(至少是面积比)实现；所述光学
 10 透光性基底由玻璃化转变点(T_g)在 80°C 和 160°C 之间的热塑性树脂制成；所述的反射薄膜是金属的，系 $300\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大导热系数的金属，而记录标记的薄膜厚度为 50nm 或更厚。

(2)按照(1)的光学记录介质，其中所述的反射膜材料的特征在于导热系数和薄膜厚度的乘积是 $2\times 10^5\text{W}\cdot\text{K}^{-1}$ 或者更大。

15 (3)一种光学记录介质，具有记录层，其首要成分是染料，位于光学透光性基底上，该介质可通过照射激光光束在所述的记录层上形成记录标记而记录信息，并通过在记录标记上照射读取激光束而读取记录的信息；其中所述的记录层具有潜在记录单元，沿激光束和记录层之间相对移动方向确定该单元任意单元长度，沿所述移动方向的正交方向确定该单元宽度，并且沿所述移动方向不断地安置；根据调整的激光束照射时间或者照射功率，以五级或更多级在所述记录层的所述潜在记录单元中可形成各种大小的记录标记；这允许多级记录五级或更多级的信息，通过调节以所述记录标记对所述潜在记录单元面积比为基础的反射比和透射比(至少是面积比)实现；所述记录层采用的染料以这样的方式制备出，
 20 即要使其由于热分解(T_g)的重量减轻开始温度，与其重量变为开始重量的 20% 时温度之差延续 100°C 范围或者更宽。

在本发明中，采用具有 $300\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 导热系数的材料作为反射膜材料，或者设置 50nm 或更薄的反射膜厚度，会导致过热，引起基底的变质或引导激光的槽切入基底以及导致记录信号降级的反射膜上的保护膜的变质。
 30

这种作用取决于导向槽所在的基底材料的玻璃化温度。当采用具有高玻璃化温度的材料，例如玻璃，作为该材料时，则由热引起的变形并不明显。如果用玻璃化温度在 80°C 和 160°C 之间的材料，发现这种效果非常明显。

5 在沿记录方向以紧相邻的各记录标记进行多级记录期间，这种热扩散影响亦被证实特别大。

这些影响由于目前为止采用的光学记录介质进行记录时发生的热而存在。然而，由于为提高多级记录法中的记录密度，记录标记沿线性方向紧挨着放置，人们认为甚至更容易发生更大的影响。

10 进一步而言，当由于激光束照射改变了其折射率使构成记录层材料分解和变质，或者折射率改变，因厚度方向尺寸引起的透射比改变时，这里陈述的记录标记的大小关系到其量变化的大小。

本发明中，通过规定构成记录层的染料而以多级方式控制反射比。

进一步而言，这种光学记录介质可如下构成。

15 (4)按照(3)的光学记录介质，其中所述的染料的特征在于，因所述热分解所致重量减少于 300°C 或更低温度开始，并持续至 350°C 或更高。

(5)按照(3)的光学记录介质，其中反射膜设置于所述记录层上与激光入射侧相对的一侧，所述的光学透光性基底是由玻璃化转变点(Tg)在 80 °C 和 160 °C 之间的热塑性树脂制成；所述的反射薄膜是金属，其具有 20 300k/W·m⁻¹·K⁻¹ 或者更大的导热系数，而记录标记上薄膜厚度为 50nm 或更厚。

(6)按照(5)的光学记录介质，其中所述的反射膜材料的特征在于，导热系数和薄膜厚度的乘积是 2×10^{-5} k/W·K⁻¹ 或者更大。

(7)按照(4)的光学记录介质，其中反射膜设置于所述记录层上与激光入射侧相对的一侧，所述的光学透光性基底是由玻璃化转变点(Tg)在 80 °C 和 160 °C 之间的热塑性树脂制成；所述的反射薄膜是金属，其具有 25 300k/W·m⁻¹·K⁻¹ 或者更大导热系数，而记录标记上薄膜厚度为 50nm 或更厚。

(8)按照(7)的光学记录介质，其中所述的反射膜材料的特征在于，导 30 热系数和薄膜厚度的乘积是 2×10^{-5} k/W·K⁻¹ 或者更大。

(9)按照(1)-(8)任一项的光学记录介质，其中所述的潜在记录单元的单元长度设置成几乎等于由激光束以最长时间照射形成的记录标记的长度。

5 (10)按照(1)-(9)任一项的光学记录介质，其中：引导激光束的导槽沿所述的记录层提供，所述的潜在记录单元位于所述槽的里面，所述单元宽度与所述槽的宽度相称。

(11)按照(1)-(10)的任一项的光学记录介质，其中所述潜在记录单元的单元长度等于或小于所述读取激光束的束腰的直径。

10 (12)按照(1)-(11)的任一项的光学记录介质，其中在所述记录层一部分上预先按多级方式记录信息。

(13)按照(1)-(12)的任一项的光学记录介质，其中至少在一个所述潜在记录单元和多级记录部分中，记录代表多级记录介质的特定信息。

(14)按照(1)-(13)的任一项的光学记录介质，其中引导激光束的导槽沿所述记录层提供并切入中部。

15 附图简介

图 1 显示本发明实施方案的光学记录介质的主要部分的局部横截面透视图。

图 2 显示采用激光束在光学记录介质中记录信息的光学记录装置的方框图。

20 图 3 显示记录标记、潜在记录单元和记录层上通过光学记录装置形成记录标记时其光学反射比之间关系的模型图。

图 4 是显示照射垂直记录单元的激光束形成另一形状时的情形的局部透视图。

本发明优选实施方案

25 参考附图，详细地介绍本发明的实施方案。

按照本发明实施方案的光学记录介质 10 是 CD-R，它采用位于记录层 12 上的染料，并由以下部分组成：包括透光性基底材料的光学透光性基底 14，由染料组成的记录层 12，涂覆并覆盖于为引导激光束在光学透光性基底 14(图 1 的上表面)表面形成的槽 16 上，首要成分是金或银或合金的、在记录层 12 上面以溅射或真空镀膜法制成的反射膜 18，和覆盖在

反射膜 18 外部的保护层 20。表示信息的不平整形状(预置槽、坑)，例如槽 16 或者寻址信号，形成在光学透光性基底 14 上。

光学透光性基底 14 是具有 80°C 和 160°C 之间玻璃化转变点的(T_g)热塑性树脂，并可以从各种类型常规光学记录介质中使用的材料中自由选择。例如，可以采用的树脂包括聚碳酸酯树脂、聚甲基丙烯酸甲酯树脂、环氧树脂、聚烯烃树脂和聚酯树脂。进一步地，玻璃化转变点例如通过 JIS K7121 介绍的差示热分析法校准。

在光学透光性基底 14 上的记录层 12 的主要成分是有机染料。这里可以采用的有机染料包括花青染料、squarylium 染料、croconium 染料、10 葱醌染料、含金属偶氮染料、酞青染料和萘醌染料。这些不同染料之中，可以采用这样的染料，即其在惰性气体保护下热分解(TG)的重量减少开始温度和重量减少至开始重量的 20% 时的温度之差延续 100°C 或更大范围。此外，由于热分解其重量减少在 300°C 或更低温度开始，持续至 350 °C 或更高。

15 染料分解温度可通过引入各种类型的极性基团来控制，它包括烷基、烷氧基、烯丙基、卤原子、烷基羰基、烷基磺酰基、烷基磺酰氨基、氰基和硝基，或者通过改变离子染料中的反离子组成来加以控制。

20 下列材料可用作有机染料涂料溶液的溶剂：酯，例如乙酸丁酯和乙酸溶纤剂；酮，例如甲乙酮、环己酮和甲基异丁基酮；氯代烃，例如二氯甲烷、1,2-二氯乙烷和氯仿；酰胺，例如二甲基甲酰胺；烃，例如环己烷；醚，例如四氢呋喃、乙醚和二噁烷；醇，例如乙醇、正丙醇、异丙醇、正丁醇和双丙酮醇；氟代溶剂，例如 2,2,3,4-四氟丙醇；和乙二醇醚，例如乙二醇单甲基醚、乙二醇单乙基醚和丙二醇单甲基醚。考虑到采用的有机染料的溶解度，这些溶剂可以单独或组合使用。根据目的不同，25 各种类型的添加剂，例如单线态氧淬灭剂、抗氧化剂、UV 吸收剂、增塑剂或润滑剂，可进一步加入到涂料溶液中。

记录层 12 上的反射膜 18 是常温(约 20°C)下具有 $300\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大导热系数的金属。这种金属是金、银或铜，或者它们的合金。反射膜 18 通过溅射法或真空镀膜法制备。反射膜 18 在形成记录标记(以后描述)处的厚度是 50nm 或者更厚，优选 60-300nm 厚度。进一步地，用于反

射膜 18 的材料其导热系数和薄膜厚度之积是 $2 \times 10^{-5} \text{ k/W}\cdot\text{K}^{-1}$ 或者更大。

保护层 20 设置于反射膜 18 之上，以物理和化学方式保护有机染料记录层 12 和反射膜 18。保护层也用于提高光学透光性基底 14 无有机染料记录层 12 一侧的抗刮擦性和额外的耐湿性。

5 通常, UV 固化树脂广泛用作保护层 20 的材料。在溶解于适当溶剂中配制出 UV 固化树脂的涂料溶液之后, 保护层 20 通过涂布该涂料溶液至光学透光性基底 14 上制成, 于是照射紫外光以固化该溶液。取决于目的, 各种不同的添加剂, 例如防静电添加剂、抗氧化剂和紫外吸收剂可加入至此涂料溶液中。保护层 20 的厚度大约是 0.1-100μm。

10 通过如图 2 所示的光学记录仪器进行以这种方式获得的光学记录介质 10 上的多级记录。

采用，例如半导体激光束作为具有 770-790nm 波长或 630-660nm 波长的记录光，通过照射适合的激光束至有机染料记录层 12 上使有机染料变质，同时光学记录介质 10 以固定的线速度或者固定的角速度旋转，进行光学记录介质 10 上的记录。通过读取有机染料变质面和未变质面反射激光量之差进行数据再生。

光学记录仪器 30 是 CD-R 记录器。此记录器这样记录信息，借助于激光器 36 的激光束，同时通过主轴马达 32 经主轴伺服装置 31 以固定的线速度或固定的角速度旋转光学记录介质(碟)10，在如上所述的光学记录介质(碟)10 上形成的记录层 12 上记录信息。

根据要记录的信息，对于如图 1 和图 3 所示的每个潜在记录单元 40(以后描述)设计激光器 36，采用激光驱动器 38 以控制激光束照射时间，即激光脉冲的数量。

图 2 的参考号 42 指包括物镜 42A 和半反射镜 42B 的记录光学系统。

25 通过聚焦跟踪伺服装置 44 进行聚焦跟踪控制,以便物镜 42A 聚焦激光束在记录层 12 上。进一步地,通过馈入伺服装置 46 控制并以固定速度从外周向内周移动物镜 42A 和半反射镜 42B,同时伴随碟 10 的旋转。

通过控制仪器 50 控制主轴伺服装置 31、激光驱动器 38、聚焦跟踪伺服装置 44 和馈入伺服装置。记录层 12 上记录的数据(信息)进入到控制仪器 50。

下一步，描述潜在记录单元 40 和潜在记录单元 40 上的记录标记。

规定这些潜在记录单元的单元宽度沿记录介质的径向，单元长度沿转动方向。单元宽度等于或小于激光束束腰直径，并可从碟 10 的道距或槽宽范围中自由选择。

5 如图 1 所示，此实施方案的潜在记录单元 40 认为连续环绕槽 16 内，并且沿碟 10 圆周转动方向具有短于束直径 D(束腰的直径)的长度(周长)。此外，设置其宽度等于槽 16。如图 3 标准样式所示就待记录的信息作出反应，照射激光束在每个潜在记录单元 40 上形成记录标记 48A-48G。

10 这里，从激光器 36 发射的激光束的束腰直径 D 在记录层 12 部位比在潜在记录单元 40 的大。然而，取决于记录层 12 选择的材料，随激光照射时间，(在激光束的中心形成具有不同直径的记录标记 48A-48G(尽管激光束是圆形的，但由于光束照射同时光学记录介质在旋转，对照射时间作出反应时记录标记形成长圆形。))。

15 由于聚焦的激光束通常形成高斯分布，在记录层 12 上仅超过激光束照射能量阈值的部分，才进行记录。由于此原因，可在记录介质中记录的激光束光点直径随激光束照射时间的变化而变化。例如，这可形成如图 3 所示的七级记录标记 48A-48G。

20 这里，组成记录层 12 的染料是如上所述加以确定的。由于与激光束照射时间有关的分解和变质不会迅速发生，良好的多级记录是可行的。

各记录标记 48A-48G 大小的设置，要使反射光的反射比在读取激光束照射潜在记录单元 40 时变成七级。当记录标记变小时反射比变大，未形成记录标记的潜在记录单元有最大反射比，形成最大记录标记 48G 的潜在记录单元的反射比最小。

25 更详细地说，(反射比的设定要考虑到与潜在记录单元 40 相关的每一个记录标记 48A-48G 的面积比，以及记录标记本身的透射比。)

记录标记 48A-48G 本身的透射比不同，因为组成记录层 12 的材料由于激光束的照射分解和变质改变了折射率，或者因为记录层 12 厚度方向的数量变化。如果形成记录标记部分的透射比是 0，就无需这种考虑。

30 此时， $300\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 或者更大导热系数的材料用作反射膜 18 的材

料。反射膜 18 的厚度是 50nm 或者更厚。进一步来说，具有 80°C 和 160°C 之间的玻璃化转变点(Tg)的材料被用于光学透光性基底 14。从而，不存在因激光束照射过度的热所导致的光学透光性基底 14 变形，使用于引导激光的槽 16 切入光学透光性基底 14 或者反射膜 18 上的保护层 20 变质。因此，记录信号不会降级。

在上面描述的实施方案中，尽管是以五级或更多级改变激光束的照射时间，以在记录层 12 上进行多级记录，但本发明并不限制于此。激光束的照射功率，或者照射时间与照射功率均可以改变。

尽管在此实施方案中，光学记录介质 10 是如上所述的 CD-R 碟，本发明并不限制于此，并且通常可以应用其它的光学记录介质。

在上述实施方案中的实施例是有关光学记录介质 10 的实施例，在其中并不记录信息，例如数据，当然本发明并不限制于此。本发明也可应用以五级或更多级记录多级信息的光学记录介质。

此外，记录层 12 中的潜在记录单元 40 的大小，当通过光学记录仪器 30 形成记录标记时，并不局限于本实施方案的实施例中，而是可以等于或小于激光束束腰直径的任一长度。

此外，尽管对于不具有槽 16 的光学记录介质可自由设置垂直记录元件 40 的大小，但优选设置垂直记录元件 40 至几乎等于形成的记录标记的长度，该记录标记是当激光束最长照射时间点的照射能超过导致记录层 12 变化的阈值时形成的。

上述的激光束在记录层 12 的位置形成圆形。然而，如图 4 所示，这可利用，例如，除了物镜 42A 之外的波束成形棱镜 42C，使波束形状沿记录介质 10 的馈入方向缩短，而呈长椭圆形或者与其成直角的线性形状。对于这种情形，由于记录标记 49 缩短，潜在记录单元也可制得更短。换言之，记录的密度可以提高。

如图 1 参考号 52 所示，通过预先设置具有大量与信号调制级数目匹配的各种反射比的若干凹坑，或者如上所述预先在一部分的光学记录介质进行多级记录，记录介质 10 具有独立识别这些若干凹坑 52 的记录标记 54 和/或完成多级记录的部分的记录介质的信息，识别用于多级记录的光学记录介质的信息，以及特定的信息，例如决定对记录/再生记录介质

必需的激光束功率的信息。这些特定的信息通过光学记录介质的再生和/或读取记录的数据，可以可靠地识别用于多级记录的光学记录介质，并且根据已经记录的凹坑数目，独立识别这些和决定激光束功率级别的数目。由于这种原因，甚至更可靠地多级记录和再生也是可能的。除了这点之外，如图 1 的参考号 56 标明的，通过提供在中部切断激光束引导槽的槽中断部分，达到同样的作用。这些方法可以独立或组合使用。

〔实施例〕

下面就本发明的实施例 1-9，与比较例 1-6 对照进行详述。这里利用在记录层 12 上采用染料的 CD-R 作为光学记录介质 10，以进行多级记录的实验。

〔实施例 1〕

将花氰染料溶解入氟代乙醇，以制备用于形成记录层的 2% 涂料溶液。采用旋涂法，其中每分钟转速从 200rpm 改变至 5000rpm，以将这种涂料溶液涂布到光学透光性基底的预制槽一侧的表面，该基底具有 120mm 直径、厚度为 1.2mm，它由聚碳酸酯树脂(Teijin Kasei Inc.: Panlight AD5503)组成，其中通过注塑法制备螺旋形预制槽(道距: 1.6μm，预制槽宽度 0.35μm，预制槽深度 0.18μm)。这种方法制成的有机染料记录层从预制槽里面的底部算起大约 200nm 厚。聚碳酸酯的玻璃化温度是 140℃。

下一步, 利用溅射法在有机染料记录层上形成 50nm 厚的 Ag(银的导热系数是 $427\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$; 科学年表)反射膜。此外, 采用每分钟转速从 300rpm 变至大约 4000rmp 的旋涂法, 在此反射膜上涂布 UV 固化树脂 (Dainipoo Ink Kagaku Kogyo Inc.: SD318)。涂布完成之后, 通过水银灯紫外线照射至涂布的薄膜上以形成 10 μm 厚的保护层。

接着采用以这种方法得到的记录介质进行多级记录。通过以六个级别改变激光束照射光学记录介质的时间，进行多级记录，同时以固定线速度旋转光学记录介质。通过照射 1mW 的激光束同时以同样的固定线速度旋转光学记录介质进行再生，接着检测光的反射量之差。用于评价记录的装置是 DDU(激光波长=784nm)，Pulstec 工业有限公司制造，记录时激光束的功率是 14mW，记录的线速度是 4.8m/秒，记录的时钟频率是 4MHz(250 纳秒)。

在光学记录介质上记录时，激光照射时间是(1)50 纳秒、(2)80 纳秒、(3)110 纳秒、(4)140 纳秒、(5)170 纳秒和(6)200 纳秒，以进行多级记录。在碟旋转一个周期内记录每个信号。

当以这种方式完成记录，并采用 Le Croy Corp. 制备的数字示波器 5 LC-534EL 读取和测量记录信号的不稳定性值时，记录时因激光束照射时间差异引起的波动很小，并得到良好的结果。

考虑到本文使用的不稳定性值测量仪器中采用常规的二元记录和再生方法，如果信号不稳定性值是 10% 或更小，判断是否进行了良好的记录是可能的。

10 [实施例 2]

如实施例 1 以同样的方式制造光学记录介质并进行多级记录，只是 Ag 反射膜的薄膜厚度改变至 100nm。记录条件与实施例 1 相同，记录信号的不稳定性值以同样方法测量。

[实施例 3]

15 如实施例 1 以同样的方式制造光学记录介质并进行多级记录，只是反射膜的材料改变成 Au(金的导热系数是 $318\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ；科学年表)。记录条件与实施例 1 相同，记录信号的不稳定性值以同样方法测量。

[实施例 4]

20 如实施例 3 以同样的方式制造光学记录介质并进行多级记录，只是反射膜的薄膜厚度改变至 100nm。记录条件与实施例 1 相同，记录信号的不稳定性值以同样方法测量。

[实施例 5]

25 如实施例 1 以同样的方式制造光学记录介质并进行多级记录，只是反射膜的材料改变成 Cu(铜的导热系数是 $401\text{k/W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ；科学年表)。记录条件与实施例 1 相同，记录信号的不稳定性值以同样方法测量。

[实施例 6]

如实施例 1 以同样的方式制造光学记录介质并进行多级记录，只是光学透光性基底材料变成聚烯烃(Zeon Corp.:ZEONEX280)。

聚烯烃的玻璃化温度是 123°C 。

30 记录条件与实施例 1 相同。

记录信号的不稳定性值以同样方法测量。

[比较例 1]

如实施例 1 以同样的方式制造光学记录介质并进行多级记录，只是 Ag 膜的薄膜厚度改变至 40nm。

5 如果以同样方法测量记录信号的不稳定性值时，当激光照射时间很长时特别发现了信号质量的问题。

[比较例 2]

如实施例 5 以同样的方式制造光学记录介质并进行多级记录，只是 Cu 膜的薄膜厚度改变至 40nm。记录信号的不稳定性值以同样方法测量。

10 [比较例 3]

如实施例 2 以同样的方式制造光学记录介质并进行多级记录，只是反射膜的材料改变成 Al(铝的导热系数是 $237\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ；科学年表)。

记录信号的不稳定性值以同样方法测量。

[比较例 4]

15 以同样的方式制造光学记录介质并进行多级记录，只是基底材料改变成玻璃。玻璃上的预制槽与实施例 1 的相同，采用等离子体蚀刻法作为形成该槽的方法。记录信号的不稳定性值以同样方法测量。

上述结果中，记录信号的不稳定性值、反射膜的特征和激光照射时间之间的关系如表 1 所示。

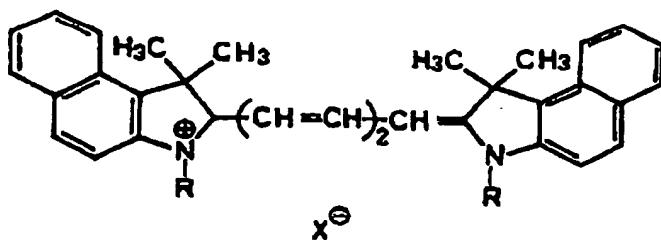
[表 1]

		实施例						比较例			
		1	2	3	4	5	6	1	2	3	4
反射膜	银	银	金	金	铜	银	银	铜	铝	银	
厚度(nm)	50	100	50	100	50	50	40	40	100	40	
薄膜厚度 × 导热系数	2.1	4.3	1.6	3.1	2.0	2.1	1.7	1.6	2.4	1.7	
基底	PC	PC	玻璃								
照射时间											
信号 不稳定 性值	(1)	6.9	5.8	7.9	7.2	7.5	7.0	9.5	10.1	9.7	7.4
	(2)	7.2	5.9	8.2	7.5	8.1	7.4	10.5	10.8	10.1	7.4
	(3)	7.4	6.2	8.4	7.6	8.4	7.7	11.5	11.7	10.7	7.6
	(4)	7.9	6.4	8.8	7.9	8.6	8.1	11.8	12.8	11.4	7.7
	(5)	8.1	6.6	9.5	8.1	8.8	8.5	12.4	13.5	12.4	8.0
	(6)	8.4	6.9	9.8	8.5	8.9	8.8	12.9	14.1	12.7	8.1

5 [实施例 7]

在与实施例 1 相同的条件下制备大约 200nm 厚的有机染料记录层，其中采用如以下化学式所示的花青染料 A。采用下述基底用作这里的光学透光性基底，即其上面预先记录有表明光学记录介质用于多级记录的差别信号和与激光束照射时间有关的信息信号。

[化学结构式 1]



R: 烷基

5

下一步，利用溅射法在有机染料记录层上制备大约 100nm 厚的 Ag 反射层。采用每分钟转速从 300rpm 变至大约 4000rmp 的旋涂法，在此反射膜上涂布 UV 固化树脂(Dainipoo Ink Kagaku Kogyo Inc.: SD318)。在涂布完成之后，通过水银灯紫外线照射至涂布的薄膜上以形成 10μm 厚的保护层。

在与实施例 1 相同的条件下将以这种方式获得的光学记录介质进行多级记录，并测量信号的不稳定性值，当记录时，因激光束照射时间差异引起的波动很小，并得到良好的结果。

采用由 TA 仪器公司制造的 2050 测量装置，在氮气中以 10°C/分钟 15 升温方式，进行花青染料 A 的热分解温度测量时，分解开始温度是 230 °C，并且当其重量变成开始重量的 20% 时温度是 480°C(分解结束温度)。进一步而言，花青染料中因热分解所致重量减少，在 300°C 或更低开始，接着持续直至 350°C 或者更高。

[实施例 8]

20 在与实施例 1 相同的条件下制备光学记录介质并进行多级记录，只是实施例 7 中的染料变成花青 A 和酞青 B 染料 1:1(摩尔比)的混合物，涂料溶剂从氟代乙醇变成乙基溶纤剂。

记录时的激光束功率设为 13mW，此时的线性记录速度是 4.8m/s，记录的时钟频率是 4MHz(250 纳秒)。记录时的激光照射时间是(1)50 纳 25 秒、(2)70 纳秒、(3)90 纳秒、(4)110 纳秒、(5)130 纳秒和(6)150 纳秒。

在碟旋转一个周期内记录每个信号。当以这种方式完成记录，并采用 Le Croy Corp. 制备的数字示波器 LC-534EL 读取和测量记录信号的不稳定性值时，记录时因激光束照射时间差异引起的波动很小，并得到良好的结果。

5 进行染料混合物的热分解温度测量期间, 分解开始温度是 230°C, 分
解结束温度是 480°C。进一步而言, 染料混合物中因热分解所致重量减少
在 300°C 或更低开始, 接着持续直至 350°C 或者更高。

[实施例 9]

在与实施例 8 相同的条件下制备光学记录介质并进行多级记录，只是实施例 8 的染料变成花青 A 和酞青 C 染料 1:1(摩尔比)的混合物。

记录时的激光束功率设为 13mW, 此时的线性记录速度是 4.8m/s, 记录的时钟频率是 4MHz(250 纳秒)。记录时的激光照射时间是(1)50 纳秒、(2)70 纳秒、(3)90 纳秒、(4)110 纳秒、(5)130 纳秒和(6)150 纳秒。在碟旋转一个周期内记录每个信号。

15 当以这种方式完成记录，并采用 Le Croy Corp. 制备的数字示波器 LC-534EL 读取和测量记录信号的不稳定性值时，记录时，因激光束照射时间差异引起的波动很小，并得到良好的结果。

进行染料混合物的热分解温度测量期间, 分解开始温度是 230°C, 分解结束温度是 547°C。进一步而言, 染料混合物中因热分解所致重量减少在 300°C 或更低开始, 接着持续直至 350°C 或者更高。

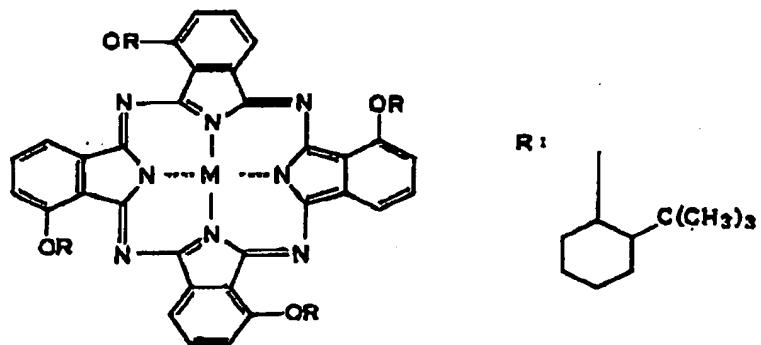
〔比较例 5〕

在与实施例 7 相同的条件下制备光学记录介质并进行多级记录，只是实施例 7 中的染料变成如以下化学结构式所示的酞青 B 染料，涂料溶剂变成乙基溶纤剂。

25 记录时的激光束功率设为 14mW, 此时的线性记录速度是 4.8m/s, 记录的时钟频率是 4MHz(250 纳秒)。记录时的激光照射时间是(1)70 纳秒、(2)80 纳秒、(3)90 纳秒、(4)100 纳秒、(5)110 纳秒和(6)120 纳秒。在一个碟旋转周期内记录每个信号。

[化学结构式 2]

M: 金属



5 当以这种方式完成记录，并采用 Le Croy Corp. 制备的数字示波器 LC-534EL 读取和测量记录信号的不稳定性值时，不管记录时光束照射时间的差异如何，发现信号不稳定性值较差。

进行酞青染料的热分解温度测量期间，分解开始温度是 319°C，分解结束温度是 414°C。

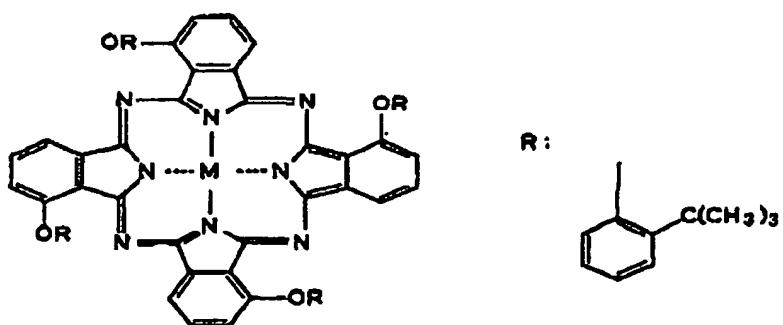
10 [比较例 6]

在与实施例 7 相同的条件下制备光学记录介质并进行多级记录，只是染料变成如以下化学式所示的酞青 C 染料，涂料溶剂变成甲基环己烷。

[化学结构式 3]

15

M: 金属



记录时的激光束功率设为 14mW，此时的线性记录速度是 4.8m/s，

记录的时钟频率是 4MHz(250 纳秒)。记录时的激光照射时间是(1)70 纳秒、(2)80 纳秒、(3)90 纳秒、(4)100 纳秒、(5)110 纳秒和(6)120 纳秒。在碟旋转一个周期内记录每个信号。

当以这种方式完成记录，并采用 Le Croy Corp. 制备的数字示波器 5 LC-534EL 读取和测量记录信号的不稳定性值时，不管记录时光束照射时间的差异如何，发现信号不稳定性值较差。

进行酞青染料 C 的热分解温度测量期间, 分解开始温度是 510℃, 分解结束温度是 546℃。

表 2 显示实施例 7-9, 比较例 5 和 6, 和以后描述的实施例 10 和 11
10 中染料的热分解特征, 记录时的激光照射时间和记录信号的不稳定性
值。

[表 2]

	实施例					比较例		
	7	8	9	10	11	5	6	
分解开始温度(°C)	230	230	230	263	242	319	510	
分解结束温度(°C)	480	480	547	820	860	414	547	
信号 不 稳 定 性 值 (%)	激光照射时间(1)	6.4	6.9	7.4	7.2	6.7	9.7	10.5
	激光照射时间(2)	6.5	7.1	7.6	7.3	6.9	9.9	11.0
	激光照射时间(3)	6.8	7.4	8.0	7.5	7.3	10.2	11.4
	激光照射时间(4)	7.1	7.8	8.5	7.8	7.5	10.7	11.4
	激光照射时间(5)	7.2	8.3	8.7	8.1	7.9	10.9	11.6
	激光照射时间(6)	7.5	8.4	9.0	8.5	8.0	11.4	12.3

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〔实施例 10〕

与实施例 1 的条件对照, 染料改变成 Ciba 制备的酞青染料[超绿]并且涂料溶剂改变成二甲基环己烷, 通过在透光性基底上形成有机染料记录层而制备光学记录介质, 该染料记录层在预制槽位置厚度大约为 20 100nm, 该透光性基底上有大约 100nm 深和约 600nm 宽的预制槽。

如表 2 所示，在与实施例 1 相同的条件下将以这种方式获得的光学记录介质进行多级记录，并测量信号的不稳定性值时，当记录时，因激光束照射时间差异引起的波动很小，并得到良好的结果。

这种染料热分解测量期间，分解开始温度大约是 263°C，分解结束温度大约是 820°C。此外，热分解所致重量减少在 300°C 或更低开始，接着持续到 350°C 或更高结束。

〔实施例 11〕

与实施例 1 的条件对照, 染料改变成 Yamada Chemicals 制备的酞青染料[YDN-02]并且涂料溶剂改变成二甲基环己烷、2-甲氧基乙醇、甲乙酮和四氢呋喃的混合物, 并且其浓度调节至 1.5wt%, 通过在透光性基底上形成有机染料记录层而制备光学记录介质, 所述染料记录层在预制槽位置厚度大约为 120nm, 所述透光性基底上有大约 160nm 深和约 650nm 宽的预制槽。

如表 2 所示，在与实施例 1 相同的条件下将以这种方式获得的光学记录介质进行多级记录，并测量信号的不稳定性值时，当记录时，因激光束照射时间的差异引起的波动很小，并得到良好的结果。

这种染料热分解测量期间，分解开始温度大约是 242°C，分解结束温度大约是 860°C。此外，热分解所致重量减少在 300°C 或更低开始，接着持续到 350°C 或更高结束。

说 明 书 附 图

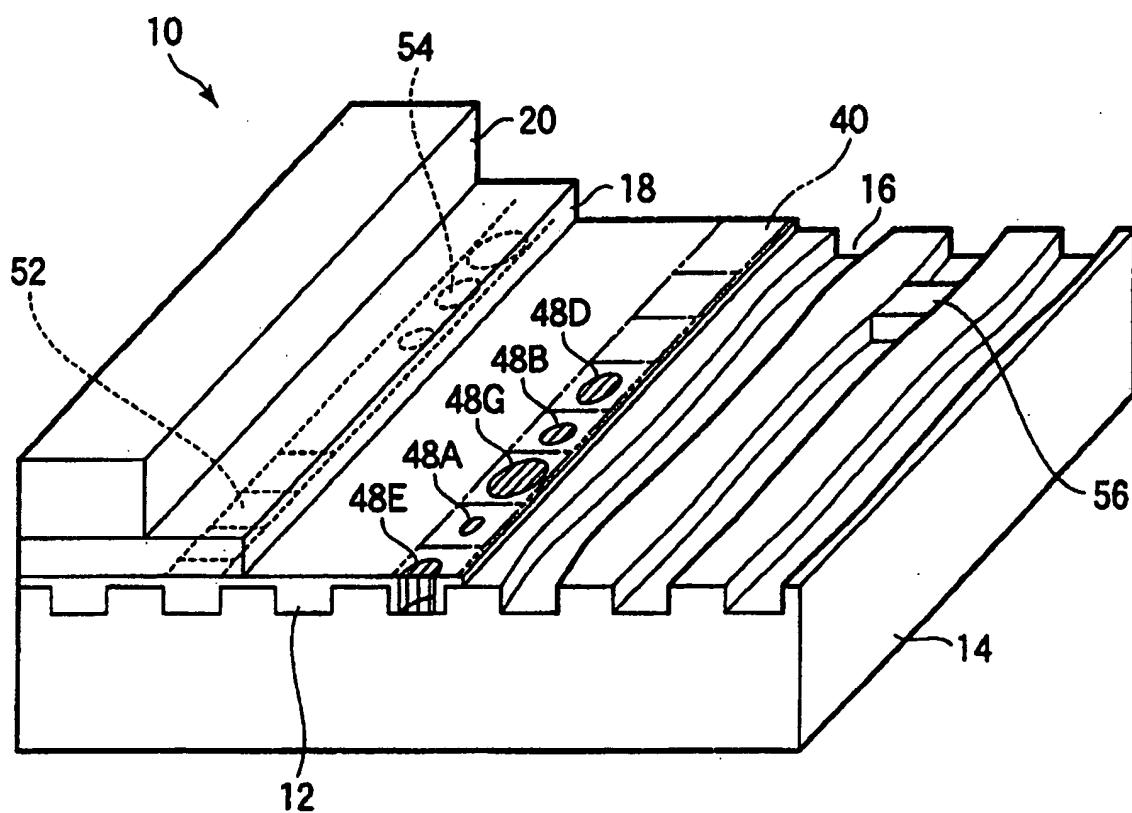


图 1

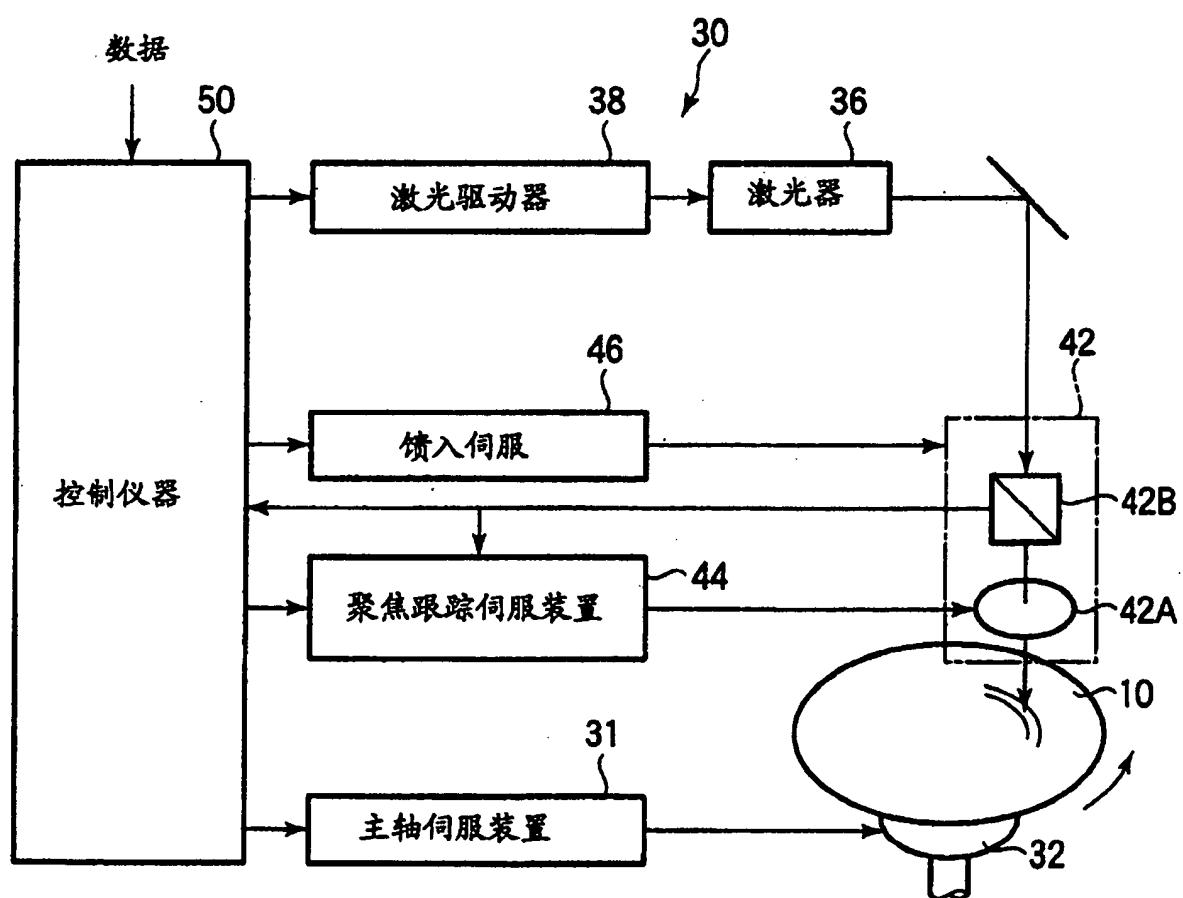
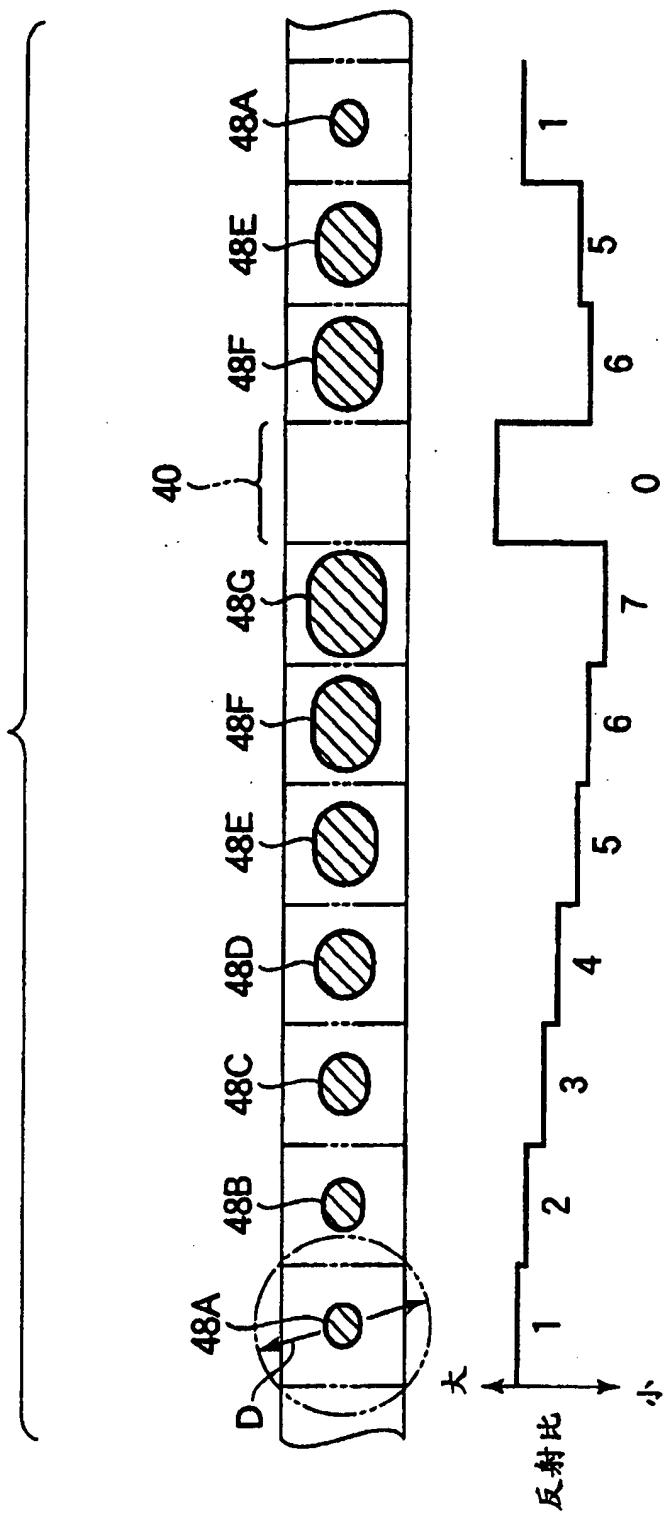


图 2



3

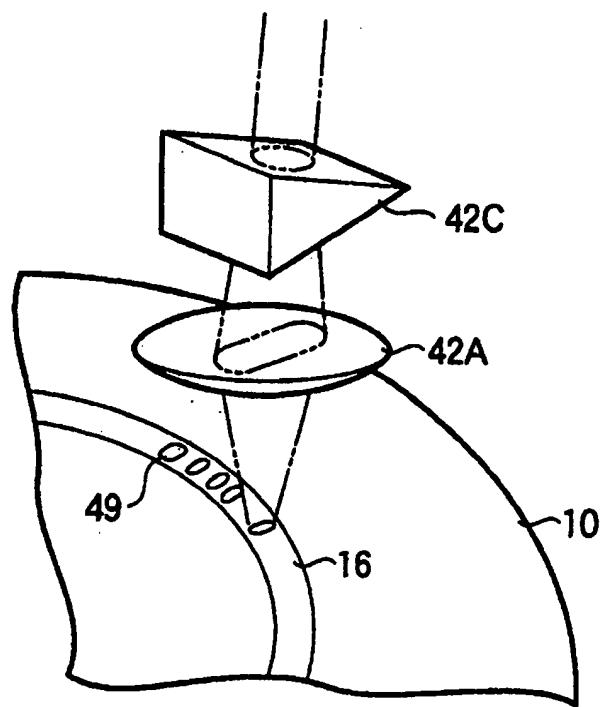


图 4

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